

## Direct Hydroxylation of Benzene Over Cu-Exchanged Hydroxy-Sodalite

Eman Z.Hegazy<sup>\*1,2</sup>, Islam H. Abd El Maksod<sup>1,2</sup>, Samia A. Kosa<sup>1</sup>, Laila M. Al-Harbi<sup>1</sup>

<sup>1</sup>King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia and

<sup>2</sup>National Research Centre, Dokki, Cairo, Egypt.

**H**YDOXYSODALITE was prepared by two different methods using normal hydrothermal heating, and using a microwave assisted the other method. Some heavy metals were selected and their removed capacity was as a probe indicator for the properties of both methods. X-ray diffraction (XRD) was used for follow-up for the crystallinity and the degree of crystal destruction upon copper ion exchange. The copper ion exchanged zeolite was used in hydroxylation of benzene as probe reaction.

The results showed that the microwave assisted prepared zeolite had lower crystallinity. Also, it showed a higher stability toward the ion exchange and higher catalytic activity per active centers.

**Keywords:** Hydroxyl sodalite, XRD, Ion exchange, EPR.

### Introduction

Phenol is considered to be one of the most important intermediate materials for manufacturing of petrochemicals, plastics and agrochemicals [1-5]. A complex cumene process usually performs production of phenol. This process uses a high consumption of energy in addition to equimolar production of acetone as a byproduct. [6]. Using H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>O or O<sub>2</sub> for direct hydroxylation of benzene into phenol becomes an economic alternative for the processing [7-11].

Hydroxysodalite(HS) is considered to be a compact cubic symmetry with Si/Al ratio of 1 [12]. The use of Hydroxylzeolite as catalyst may enhance the diffusion of reactants and products, which can enhance the catalytic activity. Copper is used as a catalyst with different oxidants in the oxidation-reduction reactions. [13-15]. The ion exchange of copper over HS will result in the presence of copper in a divalent state. The microwave is considered to be an effective alternative, and a lower cost technique for preparation of many materials [16-18].

In this paper, we will compare the preparation of HS by normal heating with the microwave assistance of two sample groups. Furthermore, we studied the stability of both samples to the extent

of copper ion exchange. The copper exchanged HS was used as an effective catalyst for direct hydroxylation of benzene into phenol. Due to the low cost of preparation of HS, we assumed that this method would have an economic impact to be used in such reactions.

### Experimental

#### Preparation of Zeolite HS

Zeolite HS was prepared from kaolin, and silica gel with alkaline hydrothermal treatment in autoclave for 5 hours at 150°C. The used autoclave was from autogenously pressure-closed autoclave. The heating was done in a normal dry oven. The Zeolite HS sample prepared previously was nominated as HS-N. The same previous composition mixture was autoclaved in the microwave at a 150°C. Moreover, the used microwave digestion system was a MileostoneE. THOS, from Italy and a 600Wattpower. This sample prepared was nominated as HS-M.

#### Catalytic activity test:

The catalytic activity was performed using 0.2 g catalyst, added to 2 mL of benzene in 16 mL of acetonitrile. After that, 3 mL of 30% H<sub>2</sub>O<sub>2</sub> was added, then the temperature was brought to 60°C for 10 minutes. The product was analyzed using a Bruker model scion 456-GC gas chromatographic

\*Corresponding author e-mail: ehgazy77@yahoo.com

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(WCOT), with a mass detector instrument. The setting for the (WCOT) fused silica was 15m x 0.25 mm injection mode, with a temperature of 260°C, rate equal to 80°C/min, and a flow equal to 1ml/min.

#### *XRD (X-ray diffraction)*

X-Ray diffractograms of various samples were collected using a Bruker D8 advance instrument with CuK $\alpha$ 1 target with second monochromator 40kV,40mA.

#### *Infrared Spectroscopy (IR)*

Infrared (IR) spectra: FTIR spectra of the samples were recorded in the range of 450–4000 cm<sup>-1</sup> on a Perkin Elmer Spectrum 100 FTIR spectrometer.

#### *Electron Paramagnetic Resonance Spectroscopy (EPR)*

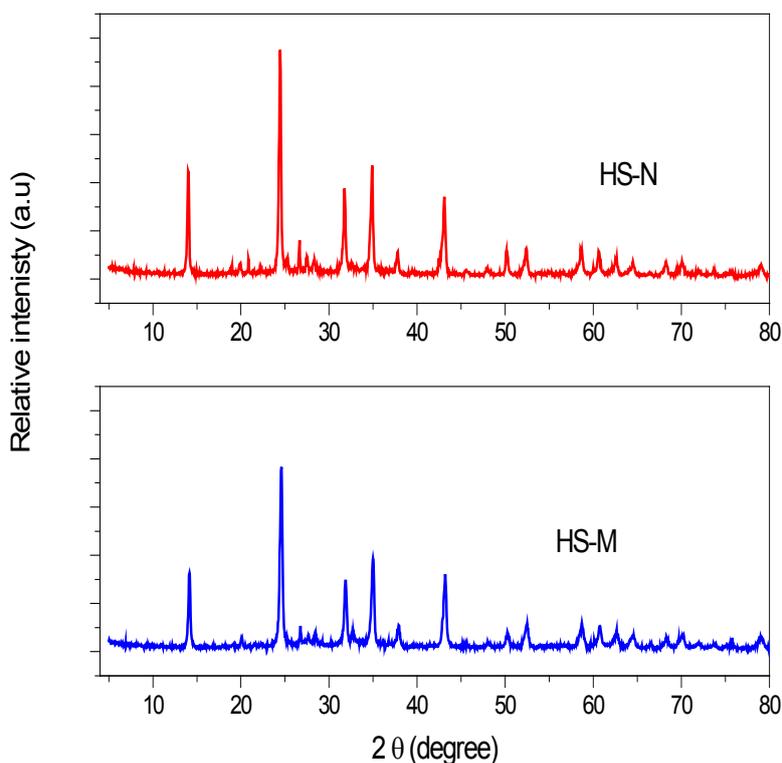
Electron paramagnetic resonance (EPR)

spectra of different solids of the catalyst were measured using (Bruker E Mex 500) operated at X-band frequency. The following parameters are generalized in all samples. The microwave frequency setting: 9.73 GHz, receiver gain: 20, sweep width: 6000 center at 3480, microwave power: 0.00202637.

### **Results and Discussion**

#### *X-ray diffraction (XRD)*

The XRD patterns of pure phases of HS are shown in Fig. 1. It shows that both samples one from microwave irradiated, and the other from normal heated have the same pure crystalline phases of HS. We can also observe that the normal heated sample is more crystalline or in other words, crystal size of microwave-irradiated sample is less than that of the normal heated one.



**Fig. 1 XRD of Normal heated and microwave irradiated samples of HS.**

Regarding the effects of ion exchange process for the copper ions on the crystal structures is concluded in Fig. of 2 and 3. As the initial concentration of copper ion increases in solution the degree of crystallinity more or less decreases.

This means the crystal lattice of HS degrades upon the increase of the initial amount of copper. It could also be observed that the stability of the microwave sample was irradiated greater than that of normal sample.

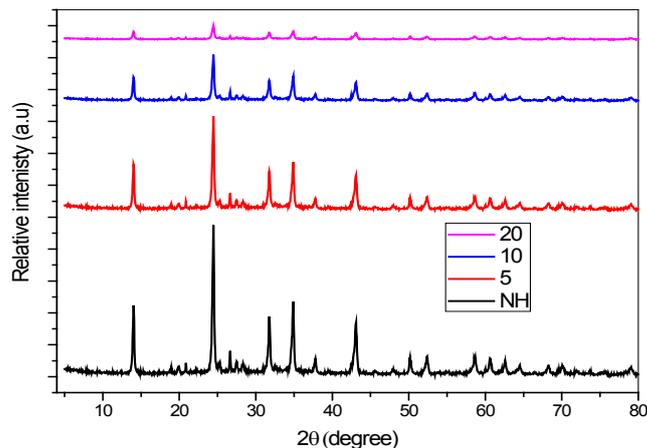


Fig.2. Effect of extent of ion exchange in XRD patterns of HS-N sample where 5, 10, 20 represents the initial concentration of  $\text{Cu}^{2+}$  in mmole.

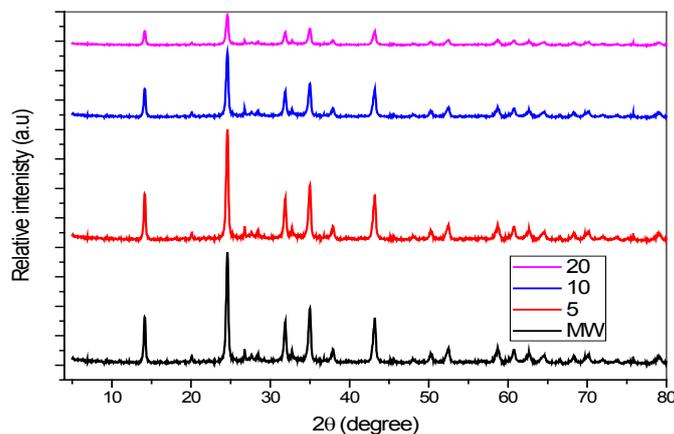


Fig.3. Effect of extent of ion exchange in XRD patterns of HS-MW sample where 5, 10, 20 represents the initial concentration of  $\text{Cu}^{2+}$  in mmole.

#### *Ion-exchange of zeolite with copper:*

Tables 1 and 2 represent the ion-exchange data of both samples. From this data, it is concluded that the maximum capacity of two samples is about  $\sim 0.7$  mmol/g. Furthermore, from the HS-N sample attained the maximum at a lower initial concentration of copper. The light of XRD patterns,

which showed that this sample had a larger crystal size, could explain this. However, the initial concentration of  $\text{Cu}^{2+}$  increases, taken from both samples. Moreover, there was a decrease of the degradation of the crystal structure of HS, which had been confirmed before by XRD patterns.

TABLE 1. Ion exchange results of microwave irradiated HS sample.

Initial amount (mmole)	Amount removed (mmole/g)
20	0.578
10	0.604
5	0.73

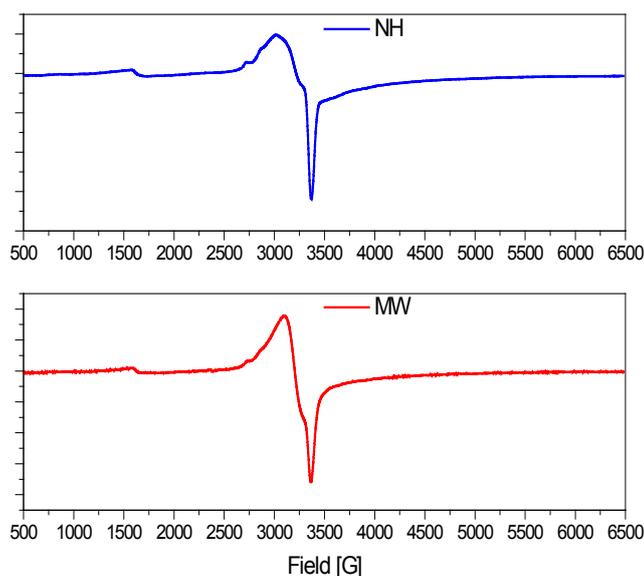
**TABLE 2.** Ion exchange results of microwave irradiated HS sample.

Initial amount (mmole)	Amount removed (mmole/g)
20	0.4
10	0.715
5	0.571

*Electron Paramagnetic Resonance Spectroscopy (EPR spectra)*

Figure 4 of the EPR spectra of both HS-N and HS-MW samples showed isotropic symmetric

signals of a copper overlap with a signal of iron impurities. This could be explained that the  $\text{Cu}^{2+}$  ions exist in symmetrical tetrahedral symmetry.

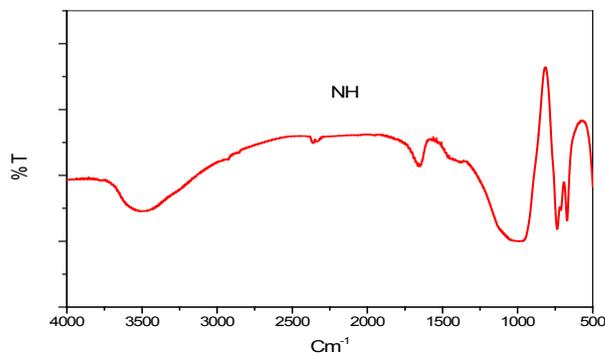


**Fig. 4.** EPR spectra of copper exchanged HS of both samples HS-N (NH) and HS-MW (MW) samples.

*Infrared Spectroscopy (IR spectra)*

Figure 5 and 6 show the IR spectra of the HS samples. They represent the typical spectra of HS

with the absence of a double ring region ( $500\text{-}650\text{ cm}^{-1}$ ), which characterizes the HS framework structure of HS.



**Fig. 5.** IR spectra of HS-NH sample.

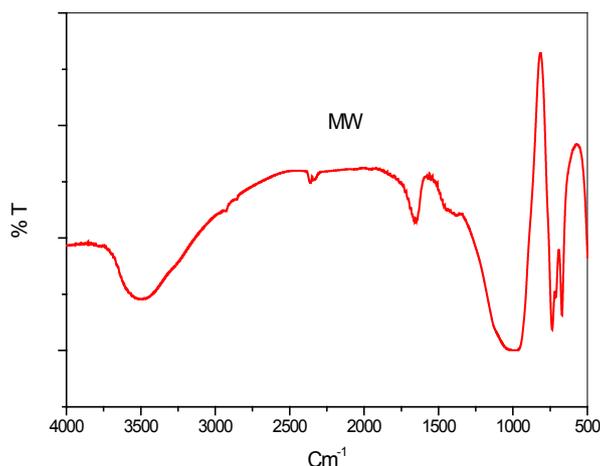


Fig. 6. IR spectra of HS-MW sample.

#### Catalytic activity of Cu-zeolite

Table 3 compares the catalytic activity from the copper amount of the zeolite samples. From the above table it could be observed that, as the degree of crystallinity of HS decreases the catalytic activity increased. In other words, the catalytic activity per active site increases.

The maximum catalytic activity reached from the HS-N sample was (159) using the least amount of Copper of (0.578 mmole/g). However, the maximum catalytic activity per active site reached for HS-MW sample was (217.5) using a Copper amount of (0.4mmole/g), which also showed a highest degree of conversion.

TABLE 3. Catalytic activity results of both sample HS-N and HS-MW in hydroxylation of phenol.

HS-N 0.2 g			HS-MW 0.2 g		
Cu- content mmole/g	% conversion	Catalytic activity per active site	Cu-content mmole/g	% conversion	Catalytic activity per active site
0.73	68%	93	0.715	60%	83.9
0.604	70%	115	0.571	68%	119
0.578	92%	159	0.4	87%	217.5

#### Conclusions

In conclusion, the Zeolite HS was successfully prepared for the first time from Saudi Arabia white silica. Also, the microwave sample was utilized as an alternative for a method of reducing time and energy in the preparation of Zeolite HS. Moreover, the microwave sample had less crystalline. Furthermore, the microwave sample showed more stability towards ion exchange. However, the copper loaded samples proved to be an excellent catalyst for hydroxylation of phenol. It only took 10 minutes with a 90% conversion, compared to a 2-hour in literature.

#### References

- 1- Min Jiang, Hai-Jun Yang, Yong Li, Zhi-Ying Jia, Hua Fu, Metal-free synthesis of substituted phenols from arylboronic acids in water at room temperature, *Chinese Chemical Letters*, **25** (5), 715-719 May (2014), ISSN 1001-8417.
- 2- Jintao Li, Lan-Lan Lou, ChenluXu, Shuangxi Liu, Synthesis, characterization of Al-rich ZSM-12 zeolite and their catalytic performance in liquid-phase tert-butylation of phenol, *Catalysis Communications*, **50** 97-100, 5 May (2014), ISSN 1566-7367, <http://dx.doi.org/10.1016/j.catcom.2014.03.011>.

- 3- SannyVerma, SangeetaPandita, Suman L. Jain, Microwave assisted synthesis of nitro phenols from the reaction of phenols with urea nitrate under acid-free conditions, *Tetrahedron Letters*, **55** (7), 1320-1322, 12 February (2014), ISSN 0040-4039, <http://dx.doi.org/10.1016/j.tetlet.2013.12.114>.
- 4- Na Guo, Yimai Liang, Shi Lan, Lu Liu, Guijuan Ji, Shucaigang, Haifeng Zou, Xuechun Xu, Uniform TiO<sub>2</sub>-SiO<sub>2</sub> hollow nanospheres: Synthesis, characterization and enhanced adsorption-photo degradation of azo dyes and phenol, *Applied Surface Science*, **305**, 562-574, 30 June (2014), ISSN 0169-4332.
- 5- Sanghapal D. Sawant, Abhinandan D. Hudwekar, K.A. Aravinda Kumar, Vunnam Venkateswarlu, Parvinder Pal Singh, Ram A. Vishwakarma, Ligand- and base-free synthesis of phenols by rapid oxidation of arylboronic acids using iron(III) oxide, *Tetrahedron Letters*, **55** (4), 811-814, 22 January (2014), ISSN 0040-4039.
- 6- Ganapati D. Yadav, Navinchandra S. Asthana, Selective decomposition of cumenehydroperoxide into phenol and acetone by a novel cesium substituted heteropolyacid on clay, *Applied Catalysis A: General*, **244** (2), 341-357, 15 May (2003), ISSN 0926-860X, [http://dx.doi.org/10.1016/S0926-860X\(02\)00605-1](http://dx.doi.org/10.1016/S0926-860X(02)00605-1).
- 7- Zhouyang Long, Yu Zhou, Guojian Chen, Pingping Zhao, Jun Wang, 4,4'-Bipyridine-modified molybdovanadophosphoric acid: A reusable heterogeneous catalyst for direct hydroxylation of benzene with O<sub>2</sub>, *Chemical Engineering Journal*, **239**, 19-25, 1 March (2014).
- 8- Liya Hu, Bin Yue, Cheng Wang, Xueying Chen, Heyong He, Enhanced catalytic activity over vanadium-containing silylated SBA-15 catalysts for styrene epoxidation and benzene hydroxylation, *Applied Catalysis A: General*, **477**, 141-146, 5 May (2014), ISSN 0926-860X.
- 9- R. Navarro, S. Lopez-Pedrajas, D. Luna, J.M. Marinas, F.M. Bautista, Direct hydroxylation of benzene to phenol by nitrous oxide on amorphous aluminum-iron binary phosphates, *Applied Catalysis A: General*, **474**, 272-279, 22 March (2014), ISSN 0926-860X.
- 10- Shoaling Song, Hongxiao Yang, Richuan Rao, Huade Liu, Aimin Zhang, Defects of multi-walled carbon nanotubes as active sites for benzene hydroxylation to phenol in the presence of H<sub>2</sub>O<sub>2</sub>, *Catalysis Communications*, **11** (8), 783-787, 31 March (2010).
- 11- Keqiang Sun, Haian Xia, Zhaochi Feng, Rutger van Santen, Emiel Hensen, Can Li, Active sites in Fe/ZSM-5 for nitrous oxide decomposition and benzene hydroxylation with nitrous oxide, *Journal of Catalysis*, **254** (2), 383-396, 10 March (2008), ISSN 0021-9517.
- 12- Milan Kanti Naskar, Debtosh Kundu, Minati Chatterjee, Coral-like hydroxysodalite particles from rice husk ash as silica source, *Materials Letters*, **65** (23-24), 3408-3410, December (2011).
- 13- Huan Liu, Changlong Yin, He Li, Bin Liu, Xuehui Li, Yongming Chai, Yanpeng Li, Chenguang Liu, Synthesis, characterization and hydrodesulfurization properties of nickel-copper-molybdenum catalysts for the production of ultra-low sulfur diesel, *Fuel*, **129**, 138-146, 1 August (2014).
- 14- Runxia HE, Haoqiang JIANG, Fang WU, Keduan ZHI, Na WANG, Chenliang ZHOU, Quansheng LIU, Effect of doping rare earth oxide on performance of copper-manganese catalysts for water-gas shift reaction, *Journal of Rare Earths*, **32** (4), 298-305, April (2014), ISSN 1002-0721.
- 15- Sk.Manirul Islam, Noor Salam, Paramita Mondal, Anupam Singha Roy, Kajari Ghosh, K. Tuhina, A highly active reusable polymer anchored copper catalyst for C-O, C-N and C-S cross coupling reactions, *Journal of Molecular Catalysis A: Chemical*, **387**, 7-19, June (2014).
- 16- Suzana Wahidin, Ani Idris, Sitti Raehanah Muhamad Shaleh, Rapid biodiesel production using wet microalgae via microwave irradiation, *Energy Conversion and Management*, **84**, 227-233 August (2014).
- 17- Wei Wang, Honglie Shen, Hanyu Yao, Jinze Li, Preparation and properties of Cu<sub>2</sub>FeSn<sub>4</sub> nanocrystals by ultrasound-assisted microwave irradiation, *Materials Letters*, **125**, 183-186, 15 June (2014), .
- 18- Wei Zhao, Jin Chen, Xiaodong Chang, Shenghui Guo, C. Srinivasakannan, Guo Chen, Jinhui Peng, Effect of microwave irradiation on selective heating behavior and magnetic separation characteristics of Panzhihuailmenite, *Applied Surface Science*, **300**, 171-177, 1 May (2014).

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## الادخال المباشر لمجموعة الهيدروكسيل في البنزين باستخدام الهيدروكسي سodalيت المحمل بالنحاس

إيمان زكريا حسين حجازي<sup>١</sup>، إسلام حمدي عبد المقصود<sup>٢</sup>، سامية عبد الحميد كوسة<sup>١</sup>، ليلي عياد الحربي<sup>١</sup>  
<sup>١</sup>جامعة الملك عبد العزيز - قسم الكيمياء - جدة  
<sup>٢</sup>المركز القومي للبحوث، قسم الكيمياء الفيزيائية- الدقي- القاهرة

تم تحضير الهيدروكسي سodalيت بطريقتين مختلفتين و تم الاستعانة بالميكروويف في احدهما. تم اختيار كمية الازالة لبعض العناصر الثقيلة كاختبار للعينات المحضرة من كلا الطريقتين. تم تتبع درجة التبلور باستخدام حيود الاشعة السينية. وتم استخدام النحاس المحمل علي الزيوليت المحضر كحفاز لادخال مجموعة الهيدروكسيل علي البنزين. أظهرت النتائج ان استخدام الميكروويف قد ادي الي درجة تبلور اقل ولكنه كان اكثر ثباتا في التبادل الأيوني كما أظهر كفاءة حفزية عالية لكل مركز نشط.